

2,3-Diaminopyridinium 6-carboxy-pyridine-2-carboxylate

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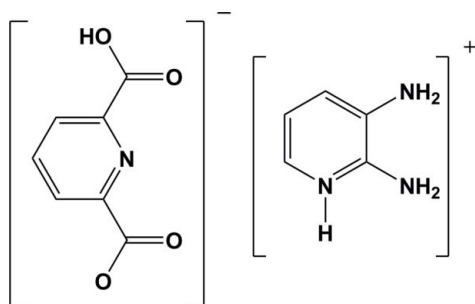
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.035; wR factor = 0.107; data-to-parameter ratio = 13.7.

The asymmetric unit of the title proton-transfer compound, $\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_7\text{H}_4\text{NO}_4^-$, consists of one mono-deprotonated pyridine-2,6-dicarboxylic acid as anion and one protonated 2,3-diaminopyridine as cation. The crystal packing shows extensive $\text{O}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds. There are also several $\pi-\pi$ interactions between the anions and also between the cations [centroid-centroid distances = 3.6634 (7), 3.7269 (7), 3.6705 (7) and 3.4164 (7) Å].

Related literature

For background to proton-transfer compounds, see: Aghabozorg *et al.* (2008*b*). For related structures, see: Aghabozorg *et al.* (2008*a*, 2011*a,b*); Sharif *et al.* (2010).



Experimental

Crystal data

$\text{C}_5\text{H}_8\text{N}_3^+\cdot\text{C}_7\text{H}_4\text{NO}_4^-$

$M_r = 276.26$

Triclinic, $P\bar{1}$
 $a = 6.9138$ (1) Å
 $b = 8.3364$ (2) Å
 $c = 11.2358$ (2) Å
 $\alpha = 81.448$ (1)°
 $\beta = 73.831$ (1)°
 $\gamma = 82.486$ (1)°

$V = 612.33$ (2) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 296$ K
 $0.24 \times 0.20 \times 0.12$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.706$, $T_{\max} = 0.746$

34839 measured reflections
2654 independent reflections
2348 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.107$
 $S = 1.07$
2654 reflections
194 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N4}-\text{H}\cdots\text{O1}^{\text{i}}$	0.86	1.94	2.7872 (12)	167
$\text{N2}-\text{H2B}\cdots\text{O3}^{\text{ii}}$	0.87 (2)	2.329 (19)	3.1108 (14)	150.0 (15)
$\text{N3}-\text{H3A}\cdots\text{O2}^{\text{i}}$	0.86	2.03	2.8674 (14)	163
$\text{N3}-\text{H3B}\cdots\text{O2}$	0.86	2.17	2.9427 (14)	149
$\text{O4}-\text{H1}\cdots\text{O1}^{\text{iii}}$	0.89 (2)	1.75 (2)	2.5673 (12)	151.9 (18)
$\text{N2}-\text{H2A}\cdots\text{O2}$	0.868 (19)	2.32 (2)	3.1290 (15)	156.0 (16)
$\text{N2}-\text{H2A}\cdots\text{N1}$	0.868 (19)	2.491 (18)	3.0999 (14)	127.8 (15)

Symmetry codes: (i) $-x + 2, -y, -z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y + 1, z$.

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5705).

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supplementary materials

Acta Cryst. (2011). E67, o3325 [doi:10.1107/S1600536811047647]

2,3-Diaminopyridinium 6-carboxypyridine-2-carboxylate

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Comment

Pyridinedicarboxylic acids are present in many natural products, such as vitamins, coenzymes, and alkaloids. Pyridine-2,6-dicarboxylic acid has been used to synthesize several proton transfer compounds in which pyridine-2,6-dicarboxylic acid acts as a monoacidic fragment (Aghabozorg *et al.* 2008b). In this regard, several organic bases were used such as propane-1,2-diamine (Aghabozorg *et al.* 2008a), *N*¹,*N*¹-dimethylpropane-1,2-diamine (Aghabozorg *et al.* 2011a), 2-amino-4-methylpyridine (Sharif *et al.* 2010) and 2-amino-4-methylpyridine (Aghabozorg *et al.*, 2011b).

The structure of the title compounds contains one deprotonated pyridine-2,6-dicarboxylic acid as anion and one protonated 2,3-diaminopyridine as cation (Fig. 1). The cations and anions are linked by several O—H···O, N—H···O and N—H···N hydrogen bonds with D···A distances ranging from 2.5673 (12) Å to 3.1290 (15) Å (Table.1 & Fig. 2). Furthermore, there are several π - π interactions which formed between (py-2,6-dcH)⁻ anions and also between (dapyH)⁺ cations with centroid-to-centroid distances = 3.6634 (7), 3.7269 (7), 3.6705 (7), 3.4164 (7) Å (Fig. 3). These hydrogen bonds and π - π interactions play important role in the stabilization of crystal packing.

Experimental

The solution of pyridine-2,6-dicarboxylic acid (0.334 g, 2 mmol) in 7 ml water was added to solution of 2,3-diaminopyridine (0.218 g, 2 mmol) in 4 ml water in 1:1 molar ratios. The reaction mixture was stirred for 3hrs at room temperature. The colorless crystals of the title compound appeared after slow evaporation of solvent at room temperature.

Refinement

The hydrogen atoms attached to O4, N2 were found in difference Fourier map and refined isotropically. The other H-atoms were included at calculated positions and treated as riding atoms: N—H = 0.86 Å for NH and NH₂, C—H = 0.98 Å for aromatic CH hydrogen atoms. These H-atoms were refined with $U_{iso}(H) = 1.2 \times U_{eq}(\text{parent atom})$.

Figures

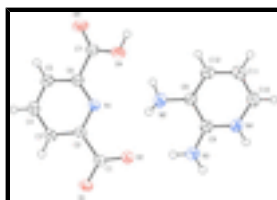


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at 50% probability level.

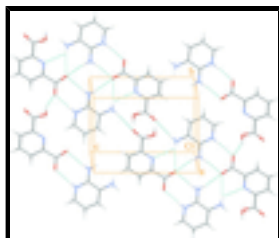


Fig. 2. The packing diagram of the title compound showing hydrogen bonding interactions as blue dashed lines.

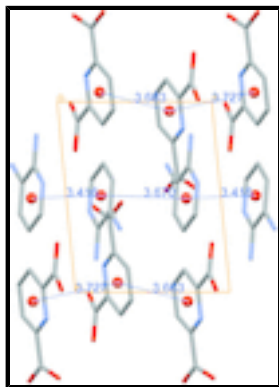
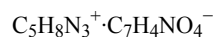


Fig. 3. The packing diagram of the title compound showing π - π interactions between (py-2,6-dcH)⁻ anions and between (dapyH)⁺ cations.

2,3-Diaminopyridinium 6-carboxypyridine-2-carboxylate

Crystal data



$M_r = 276.26$

Triclinic, PT

Hall symbol: $-P\ 1$

$a = 6.9138\ (1)\ \text{\AA}$

$b = 8.3364\ (2)\ \text{\AA}$

$c = 11.2358\ (2)\ \text{\AA}$

$\alpha = 81.448\ (1)^\circ$

$\beta = 73.831\ (1)^\circ$

$\gamma = 82.486\ (1)^\circ$

$V = 612.33\ (2)\ \text{\AA}^3$

$Z = 2$

$F(000) = 288$

$D_x = 1.498\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 9842 reflections

$\theta = 2.9\text{--}30.0^\circ$

$\mu = 0.12\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Irregular, colorless

$0.24 \times 0.20 \times 0.12\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

2654 independent reflections

Radiation source: fine-focus sealed tube
graphite

2348 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

φ and ω scans

$\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 2.5^\circ$

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$h = -8 \rightarrow 8$

$T_{\text{min}} = 0.706$, $T_{\text{max}} = 0.746$

$k = -10 \rightarrow 10$

34839 measured reflections

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.107$	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.1194P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
2654 reflections	$(\Delta/\sigma)_{\max} < 0.001$
194 parameters	$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.00070 (17)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R - factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O3	0.64901 (16)	0.46889 (11)	0.60916 (9)	0.0508 (3)
O2	0.91253 (17)	-0.01029 (10)	0.21751 (8)	0.0479 (3)
O1	0.91229 (15)	-0.25266 (10)	0.32864 (8)	0.0419 (2)
O4	0.83898 (16)	0.45238 (11)	0.41533 (8)	0.0480 (3)
C8	0.72493 (16)	0.42375 (14)	0.08478 (10)	0.0310 (2)
N4	0.85753 (15)	0.42597 (12)	-0.13478 (9)	0.0352 (2)
H	0.9115	0.3742	-0.1986	0.042*
N1	0.79718 (13)	0.13922 (10)	0.42873 (8)	0.0271 (2)
C9	0.81096 (17)	0.33895 (14)	-0.02186 (10)	0.0314 (2)
C10	0.8247 (2)	0.59072 (16)	-0.15453 (11)	0.0400 (3)
H10	0.8605	0.6451	-0.2349	0.048*
N3	0.84405 (18)	0.17690 (13)	-0.01308 (10)	0.0451 (3)
H3A	0.8947	0.1294	-0.0793	0.054*
H3B	0.8148	0.1199	0.0588	0.054*
C11	0.7393 (2)	0.67446 (15)	-0.05574 (12)	0.0417 (3)

supplementary materials

H11	0.7130	0.7872	-0.0675	0.050*
C12	0.69064 (19)	0.58993 (15)	0.06456 (11)	0.0379 (3)
H12	0.6336	0.6481	0.1324	0.045*
C7	0.73268 (17)	0.39063 (13)	0.52423 (10)	0.0319 (3)
C6	0.72505 (16)	0.20977 (13)	0.53341 (10)	0.0276 (2)
C2	0.79375 (15)	-0.02216 (12)	0.43816 (9)	0.0262 (2)
C1	0.87808 (17)	-0.10003 (13)	0.31804 (10)	0.0299 (2)
C3	0.71865 (17)	-0.11635 (13)	0.55079 (10)	0.0307 (2)
H3	0.7201	-0.2286	0.5541	0.037*
C4	0.64189 (18)	-0.04065 (14)	0.65777 (11)	0.0350 (3)
H4	0.5889	-0.1007	0.7340	0.042*
C5	0.64532 (18)	0.12568 (14)	0.64934 (10)	0.0332 (3)
H5	0.5953	0.1802	0.7197	0.040*
N2	0.67215 (18)	0.33369 (15)	0.20004 (10)	0.0402 (3)
H2A	0.755 (3)	0.253 (2)	0.2184 (16)	0.057 (5)*
H2B	0.625 (3)	0.397 (2)	0.2583 (17)	0.057 (5)*
H1	0.840 (3)	0.560 (2)	0.4101 (17)	0.067 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0713 (7)	0.0303 (5)	0.0412 (5)	-0.0035 (4)	0.0066 (4)	-0.0163 (4)
O2	0.0818 (7)	0.0281 (4)	0.0250 (4)	0.0055 (4)	-0.0045 (4)	-0.0033 (3)
O1	0.0636 (6)	0.0200 (4)	0.0345 (5)	-0.0030 (4)	0.0009 (4)	-0.0068 (3)
O4	0.0736 (7)	0.0227 (4)	0.0374 (5)	-0.0120 (4)	0.0082 (4)	-0.0080 (3)
C8	0.0314 (5)	0.0338 (6)	0.0267 (5)	-0.0006 (4)	-0.0060 (4)	-0.0059 (4)
N4	0.0408 (5)	0.0369 (5)	0.0247 (5)	0.0027 (4)	-0.0051 (4)	-0.0064 (4)
N1	0.0332 (5)	0.0206 (4)	0.0257 (4)	-0.0017 (3)	-0.0049 (3)	-0.0040 (3)
C9	0.0327 (5)	0.0319 (6)	0.0285 (5)	0.0003 (4)	-0.0071 (4)	-0.0054 (4)
C10	0.0457 (7)	0.0385 (6)	0.0311 (6)	0.0024 (5)	-0.0092 (5)	0.0028 (5)
N3	0.0653 (7)	0.0318 (5)	0.0317 (5)	0.0031 (5)	-0.0038 (5)	-0.0069 (4)
C11	0.0500 (7)	0.0299 (6)	0.0420 (7)	0.0053 (5)	-0.0121 (5)	-0.0025 (5)
C12	0.0430 (6)	0.0356 (6)	0.0331 (6)	0.0044 (5)	-0.0069 (5)	-0.0110 (5)
C7	0.0378 (6)	0.0252 (5)	0.0312 (5)	-0.0023 (4)	-0.0046 (4)	-0.0076 (4)
C6	0.0303 (5)	0.0233 (5)	0.0283 (5)	-0.0015 (4)	-0.0050 (4)	-0.0058 (4)
C2	0.0303 (5)	0.0211 (5)	0.0267 (5)	-0.0005 (4)	-0.0072 (4)	-0.0035 (4)
C1	0.0384 (6)	0.0220 (5)	0.0280 (5)	-0.0016 (4)	-0.0064 (4)	-0.0046 (4)
C3	0.0384 (6)	0.0209 (5)	0.0309 (5)	-0.0033 (4)	-0.0073 (4)	-0.0008 (4)
C4	0.0421 (6)	0.0314 (6)	0.0269 (5)	-0.0057 (5)	-0.0030 (4)	0.0011 (4)
C5	0.0395 (6)	0.0313 (6)	0.0257 (5)	-0.0022 (4)	-0.0017 (4)	-0.0077 (4)
N2	0.0489 (6)	0.0394 (6)	0.0263 (5)	0.0006 (5)	-0.0022 (4)	-0.0043 (4)

Geometric parameters (\AA , $^\circ$)

O3—C7	1.2041 (14)	N3—H3A	0.8600
O2—C1	1.2401 (14)	N3—H3B	0.8600
O1—C1	1.2574 (13)	C11—C12	1.4008 (18)
O4—C7	1.3088 (14)	C11—H11	0.9300
O4—H1	0.89 (2)	C12—H12	0.9300

C8—C12	1.3702 (17)	C7—C6	1.5028 (15)
C8—N2	1.3760 (15)	C6—C5	1.3862 (15)
C8—C9	1.4262 (15)	C2—C3	1.3903 (14)
N4—C9	1.3414 (14)	C2—C1	1.5185 (14)
N4—C10	1.3575 (16)	C3—C4	1.3811 (16)
N4—H	0.8600	C3—H3	0.9300
N1—C6	1.3343 (14)	C4—C5	1.3786 (16)
N1—C2	1.3365 (13)	C4—H4	0.9300
C9—N3	1.3338 (15)	C5—H5	0.9300
C10—C11	1.3512 (18)	N2—H2A	0.868 (19)
C10—H10	0.9300	N2—H2B	0.87 (2)
C7—O4—H1	112.4 (12)	O3—C7—C6	122.78 (10)
C12—C8—N2	124.24 (10)	O4—C7—C6	112.99 (9)
C12—C8—C9	117.42 (10)	N1—C6—C5	123.76 (10)
N2—C8—C9	118.25 (10)	N1—C6—C7	117.67 (9)
C9—N4—C10	124.00 (10)	C5—C6—C7	118.57 (10)
C9—N4—H	118.0	N1—C2—C3	122.83 (9)
C10—N4—H	118.0	N1—C2—C1	116.38 (9)
C6—N1—C2	117.28 (9)	C3—C2—C1	120.79 (9)
N3—C9—N4	119.21 (10)	O2—C1—O1	124.63 (10)
N3—C9—C8	122.31 (10)	O2—C1—C2	118.57 (9)
N4—C9—C8	118.47 (10)	O1—C1—C2	116.78 (9)
C11—C10—N4	119.02 (11)	C4—C3—C2	118.99 (10)
C11—C10—H10	120.5	C4—C3—H3	120.5
N4—C10—H10	120.5	C2—C3—H3	120.5
C9—N3—H3A	120.0	C5—C4—C3	118.73 (10)
C9—N3—H3B	120.0	C5—C4—H4	120.6
H3A—N3—H3B	120.0	C3—C4—H4	120.6
C10—C11—C12	119.37 (11)	C4—C5—C6	118.40 (10)
C10—C11—H11	120.3	C4—C5—H5	120.8
C12—C11—H11	120.3	C6—C5—H5	120.8
C8—C12—C11	121.69 (11)	C8—N2—H2A	118.7 (12)
C8—C12—H12	119.2	C8—N2—H2B	110.6 (12)
C11—C12—H12	119.2	H2A—N2—H2B	113.8 (16)
O3—C7—O4	124.23 (10)		
C10—N4—C9—N3	178.04 (12)	O3—C7—C6—C5	-10.12 (18)
C10—N4—C9—C8	-1.15 (17)	O4—C7—C6—C5	169.81 (11)
C12—C8—C9—N3	-177.65 (11)	C6—N1—C2—C3	0.21 (16)
N2—C8—C9—N3	-0.97 (17)	C6—N1—C2—C1	-179.54 (9)
C12—C8—C9—N4	1.52 (16)	N1—C2—C1—O2	-11.91 (15)
N2—C8—C9—N4	178.20 (10)	C3—C2—C1—O2	168.34 (11)
C9—N4—C10—C11	-0.31 (19)	N1—C2—C1—O1	166.52 (10)
N4—C10—C11—C12	1.3 (2)	C3—C2—C1—O1	-13.22 (16)
N2—C8—C12—C11	-176.99 (12)	N1—C2—C3—C4	0.76 (17)
C9—C8—C12—C11	-0.54 (18)	C1—C2—C3—C4	-179.51 (10)
C10—C11—C12—C8	-0.9 (2)	C2—C3—C4—C5	-0.98 (17)
C2—N1—C6—C5	-0.96 (16)	C3—C4—C5—C6	0.29 (18)
C2—N1—C6—C7	178.62 (9)	N1—C6—C5—C4	0.71 (18)

supplementary materials

O3—C7—C6—N1	170.28 (12)	C7—C6—C5—C4	-178.86 (10)
O4—C7—C6—N1	-9.79 (15)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N4—H···O1 ⁱ	0.86	1.94	2.7872 (12)	167.
N2—H2B···O3 ⁱⁱ	0.87 (2)	2.329 (19)	3.1108 (14)	150.0 (15)
N3—H3A···O2 ⁱ	0.86	2.03	2.8674 (14)	163.
N3—H3B···O2	0.86	2.17	2.9427 (14)	149.
O4—H1···O1 ⁱⁱⁱ	0.89 (2)	1.75 (2)	2.5673 (12)	151.9 (18)
N2—H2A···O2	0.868 (19)	2.32 (2)	3.1290 (15)	156.0 (16)
N2—H2A···N1	0.868 (19)	2.491 (18)	3.0999 (14)	127.8 (15)

Symmetry codes: (i) $-x+2, -y, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, y+1, z$.

Fig. 1

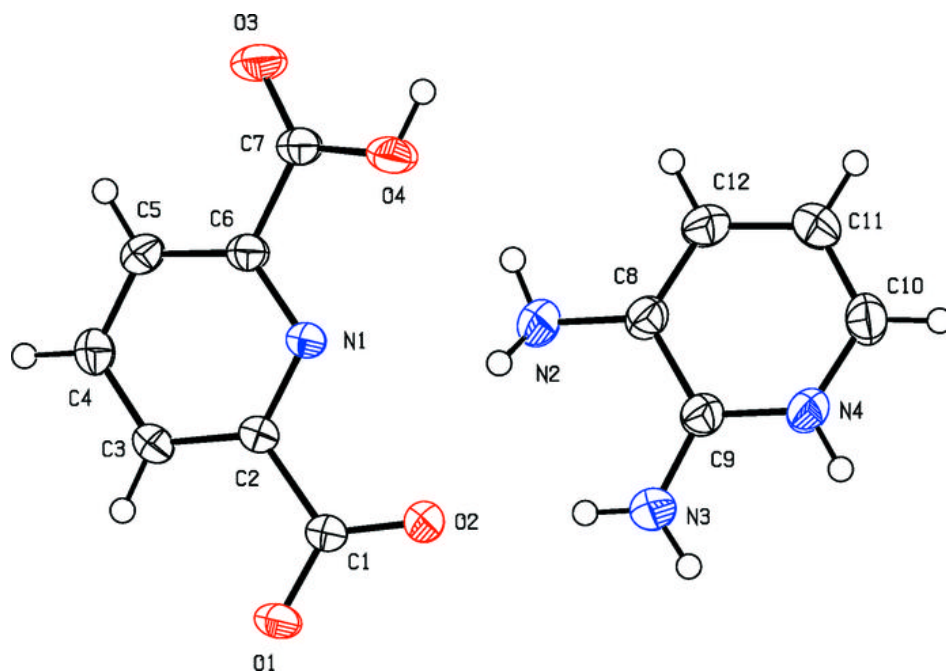


Fig. 2

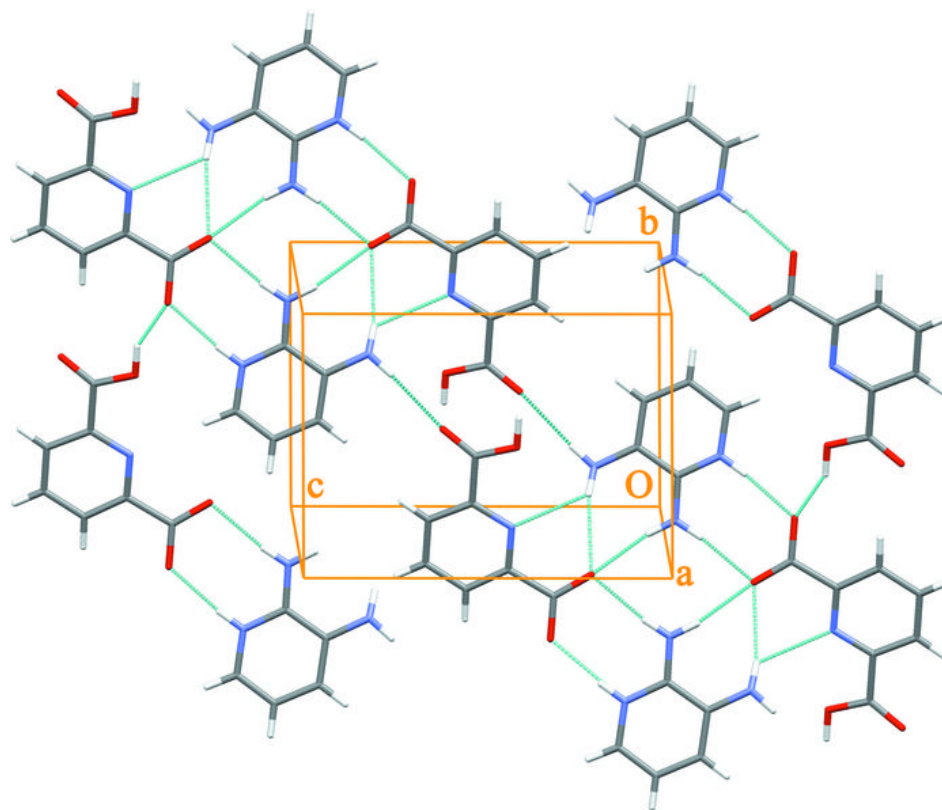


Fig. 3

